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(54) Continuous procedure for obtaining pure terephthalic acid and glycol starting from polyethylene terephthalate waste

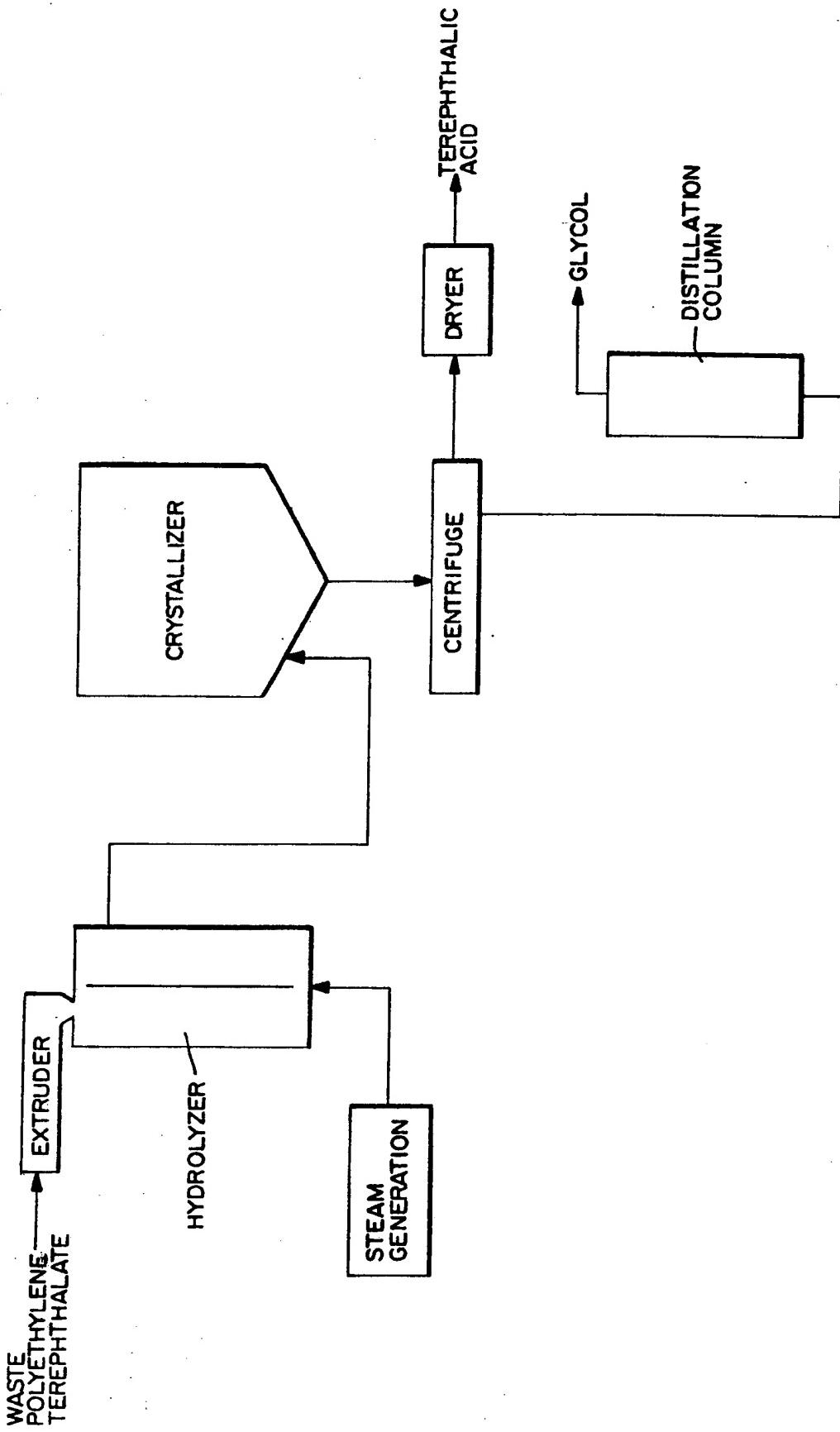
(57) A procedure is described to obtain pure terephthalic acid and glycol, which consists in carrying out, in a continuous manner and in the presence of decolorizing carbon, an aqueous and neutral hydrolysis of polyethylene terephthalate waste, under high temperature and pressure conditions, continuously filtering the product at the hydrolysis temperature and crystallizing the terephthalic acid, while the mother liquors are subjected to distillation in order to obtain the glycol.

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SPECIFICATION

Continuous procedure for obtaining pure terephthalic acid and glycol starting from polyethylene terephthalate waste

- 5 *Field of the invention*
The invention under consideration is related to a continuous method which permits obtaining pure terephthalic acid and glycol and more specifically, it is related with a procedure which utilizes as a raw material polyethylene terephthalate waste and in which it is not necessary to
10 first separate the crude or impure terephthalic acid in order to purify it in a subsequent stage by means of one of the known procedures. In the method of the invention under consideration, the product is obtained pure and can be utilized as a raw material once again in the preparation of the polyethylene terephthalate utilized in the manufacture of polyester fibers and plastics. 10
- 15 *Description of the prior art*
Neutral hydrolysis of polyethylene terephthalate at a high temperature and pressure is a known operation (see Ludewig, H. and Ramm, H.: German Economic Patent 14,854 (1956) and Littmann, E. On the preparation of terephthalic acid or its dimethyl or diglycol ester from polyethylene terephthalate. Abh. d. Deutsch. Akad. d. Wiss. Kl. F. Chem., Geolog. und Biochemie I (1963) 401–411). 15
- 20 Neither of the methods described in the aforementioned references mentions the addition of decolorizing carbon in the hydrolysis stage.
On the other hand, the methods mentioned there are discontinuous methods in which, moreover, the terephthalic acid is obtained impure so that once it is separated, it will have to be
25 subjected to some purifying procedure. 25
- 20 In this way, the methods to which reference has been made require a subsequent purifying stage which may be the dissolution of the product in sodium hydroxide and subsequently, a reprecipitation by means of acidification, either with treatment of the solution obtained or without an intermediate treatment, or by having recourse to transformation to the dimethyl ester, which is subsequently sublimed. 30
- 35 *Summary of the invention*
The method of the invention under consideration has as its object the obtaining of terephthalic acid and glycol in which the purification is undertaken simultaneously with the hydrolysis.
35 Another object of the invention under consideration is to provide a method for the preparation of pure terephthalic acid and glycol in which the number of stages of the process is reduced. An advantage of the method of the invention under consideration is that upon reducing the number of stages of the process—that is, upon eliminating the subsequent stage of purifying the terephthalic acid—the cost of the product is lowered.
40 Another advantage of the invention under consideration is that it permits the utilization of the polyethylene terephthalate in a simple manner.
Yet another advantage of the method of this invention is that due to the simplicity of the equipment utilized, it can be carried out with relative ease.
45 These and other objects of the invention under consideration will, in part, be obvious and, in part, will become more apparent as the description proceeds and with the aid of the detailed description of the invention. 45
- 50 *Detailed description of the invention*
According to the method of this invention, the polyethylene terephthalate waste is supplied in the form of granules or yarns or in any other form suitable for handling, to the melting chamber of a screw-type extruder so that the extruder, in turn, feeds it, in a continuous manner, to a hydrolyzer. Alternatively, the polymer can also be melted and injected continuously into the hydrolyzer in this state by means of a high-pressure pump.
55 In a simultaneous manner, water is injected into said hydrolyzer in a suitable proportion—that is, from 3 to 20 times the amount of the polymer. The water can be introduced cold or hot. In turn, the decolorizing carbon is added in a proportion between 0.1% and 30% (with respect to the quantity of the treated waste), feeding it to the hydrolyzer either with the polymer or suspended in water. Also, a large amount can be introduced in bulk intermittently into the hydrolyzer every so often. The hydrolyzer utilized can be of any type—that is, it can be
60 cylindrical vertical, horizontal or inclined, or it can be the U-shaped type, either vertical, horizontal or inclined. 60
- The hydrolyzer, in turn, should be equipped with a source of heating which can be a jacket

Heating can also be provided by means of live steam at high pressure, which is introduced directly into the hydrolyzer.

Preferably, the hydrolyzer should be equipped with devices which impart a slight agitation.

When the equipment is put into operation, the polymer which has not yet been hydrolyzed 5 will be found in the lower part. This is also true for the greater part of the carbon, whereas, on the other hand, the supernatant liquid will be an aqueous solution of terephthalic acid and glycol with some proportion of the decolorizing carbon utilized, which will be suspended in the solution.

This solution is subjected to a filtering operation under the temperature and pressure

10 conditions in which the hydrolysis is carried out, with the object of eliminating the carbon and all the impurities adsorbed by it. This filtration can be carried out in many diverse ways but the use of a heated cartridge filter is particularly preferred; this is located next to the hydrolyzer—that is, said filtration can be undertaken by means of cartridges which are installed directly within the hydrolyzer.

15 Once the solution is filtered, the pressure to which it is subjected is released and it is sent to a continuous crystallizer which may be at atmospheric pressure, at a pressure higher than atmospheric pressure, or at a pressure lower than atmospheric pressure.

This crystallizer can be equipped with a cooling jacket or a coil, or cooling may be attained by simply venting the pressure.

20 The magma obtained in this manner in the crystallizer is filtered continuously, either by using a filter or with a centrifuge. The crystals are washed in the same filtering device and are dried so as to be stored and recycled.

On the other hand, the filtrate of the magma, which is an aqueous glycol solution is sent to distillation equipment where the glycol is obtained in pure form.

25 The following indicates the preferred operating conditions in the method, with the upper and lower limits of the permissible conditions being indicated. The indicated parameters are not independent of one another and upon modifying one of them, it may be necessary, or at least convenient, to change one or several of the others.

30	Minimum	Maximum	Remarks	30
Water/polymer ratio	3	20	Note 1	
Carbon/polymer ratio	0.1%	30%	Note 2	
Hydrolysis temperature	200°C	300°C	Note 3	
35 Hydrolysis pressure	15 atmospheres	100 atmospheres	Note 4	35
Residence time in the hydrolyzer	5 min.	6 hours	Note 5	
Residence time in the crystallizer	5 min.	5 hours	Note 6	40
Temperature in the crystallizer	- 10°C	200°C	Note 7	

45 Note 1. The quantity of water should be sufficient so as to keep the terephthalic acid dissolved as it is being formed; such a quantity will depend on the temperature at which the hydrolysis takes place.

Note 2. The quantity of carbon needed will depend on the quantity of impurities in the polymer and the final purity desired in the terephthalic acid produced.

50 Note 3. The greater the temperature, the higher will be the rate of the reaction, with the pressure in the equipment being greater at the same time.

Note 4. The pressure is a function of the temperature.

Note 5. The residence time required will depend on the temperature used and on the morphology of the polymer.

55 Note 6. The residence time in the crystallizer will depend on the average size of the crystal desired, with the crystal being larger, the greater the residence time.

In accordance with the data previously indicated, the method of the invention can be carried out under conditions which are different up to a certain point, and it can be modified in accordance with the level of production required.

60 Also, very different heating sources can be used, with the needed changes also made in accordance with the morphology and the quality of the waste which is utilized as a raw material.

There will also be variations in accordance with the characteristics of purity and size of the crystal desired in the terephthalic acid produced.

Taking into consideration all the modifications which are comprised within the spirit and scope of the invention, the following will give the preferred embodiment, which is merely for illustrative purposes.

5 *Detailed explanation of the preferred embodiment*

In this embodiment, the method of the invention is carried out with the following equipment as illustrated in the drawing:

a) A twin-screw melter extruder which is discharged by means of a multiple-orifice spray head directly into the upper part of the hydrolyzer.

10 b) A vertical cylindrical hydrolyzer which has a vertical plate in its interior which divides the hydrolyzer into two semiconductor sections. Said plate does not have to extend along the whole length but rather will leave a free space both in the upper as well as the lower parts. The supply nozzle which is connected with the extruder is centered over one of the semicircles. On the upper part of the other semicircle there is a bundle of filter cartridges whose outlets are all 15 connected with a common discharge tube. The entry of water is on one side of the hydrolyzer, the side corresponding to the supply of the polymer. The bottom of the hydrolyzer will be equipped with two connections—one which will be used for the introduction of live steam, and the drainage of said hydrolyzer being undertaken through the other connection.

20 c) A continuous crystallizer which is made up of a vertical tank, a conical bottom and which is equipped with an agitator. The crystallizer is connected to the discharge tube of the filter 20 cartridges on the hydrolyzer by means of a line and an automatic valve which permits the passage of all the liquid in addition to a small quantity of steam which has an agitation function in the hydrolyzer. Said crystallizer also includes an automatic level control discharge device.

d) A continuous centrifuge with a washing device which receives the discharge from the 25 crystallizer and which, in turn, continuously discharges towards the drier.

e) A drier of the vibrating screen type.

f) A distillation column for the recovery of the glycol, on the basis of mother liquors.

What has been described in the preceding is related to the equipment which is particularly preferred for carrying out the method, which consists of the following stages.

30 The hydrolyzer is loaded with a suitable quantity of water in a continuous manner by means of a metering pump. High-pressure saturated steam is also injected continuously from the lower part of the hydrolyzer. The waste polymer, together with decolorizing carbon is fed continuously to the hydrolyzer by means of the extruder previously described.

The discharge from the hydrolyzer is adjusted in such a manner that it is slightly agitated by 35 means of the excess steam.

Once the hydrolysis has been undertaken, the product is subjected to filtration in order to be subsequently crystallized. One should indicate that the agitation in the crystallizer has to be the minimum so as to keep the crystals suspended.

The crystals obtained are subjected to a drying stage, which is carried out in a drier which has 40 the flow of air and the temperature suitably adjusted so that neither is excessive.

The distillation of the filtrate, in turn, is carried out in the customary manner in order to obtain the glycol pure.

For the case particularly described, the specific reaction conditions are the following:—

45	Water/polymer ratio	12	45
	Carbon/polymer ratio	10%	
	Hydrolysis temperature	248°C	
	Hydrolysis pressure	42 atmospheres	
50	Residence time in the hydrolyzer	2 hours	50
	Frequency of carbon discharge every 24 hours		
	Residence time in the crystallizer	4 hours	
	Drying temperature	80°C	

55 Although a particularly preferred embodiment has been described and certain changes which can be carried out in the method of the invention under consideration have been outlined, it is obvious that experts in the branch will be able to make, in view of the description under consideration, other modifications, without this deviating from the spirit and scope of the invention so that the preceding description should be considered only for the purposes of 55 illustration and not in any limiting sense, and the scope of this invention should be defined in terms of the following clauses:

- subject to hydrolysis, in the presence of a certain amount of decolorizing carbon, a quantity of polyethylene terephthalate waste with water, at a high pressure and at a temperature which varies between 200°C and 300°C; filter the hydrolyzate also under conditions of high temperature and pressure; crystallize the terephthalic acid of the filtered solution by means of
- 5 cooling in the crystallization receptor at a final temperature which varies between – 10°C and 5
200°C; filter or centrifuge to separate the filtrate crystals; wash and dry the pure terephthalate acid crystals; and, on the other hand, distil the filtrate so as to obtain pure glycol.
2. Continuous method for obtaining pure terephthalic acid and glycol starting from polyethylene terephthalate waste in accordance with what is claimed in clause 1, characterized
- 10 furthermore by the fact that the quantity of water used is equal or greater than that required to 10
keep the terephthalic acid dissolved under hydrolysis conditions.
3. Continuous method for obtaining pure terephthalic acid and glycol starting from polyethylene terephthalate waste in accordance with what is claimed in clauses 1 and 2, characterized also by the fact that the time of the hydrolysis reaction is between 5 minutes and
- 15 6 hours. 15
4. Continuous method for obtaining pure terephthalic acid and glycol starting from polyethylene terephthalate waste in accordance with what is claimed in clauses 1 to 3, also characterized by the fact that the quantity of the decolorizing carbon added is between 0.1% and 30%, with respect to the quantity of waste treated.
- 20 5. Continuous method for obtaining pure terephthalic acid and glycol, starting from 20
polyethylene terephthalate waste, in accordance with what is claimed in clauses 1–4, characterized also by the fact that the cooling is carried out by venting the pressure in the crystallizer.
6. Continuous method for obtaining pure terephthalate acid and glycol, starting from polyethylene terephthalate, in accordance with what is claimed in clauses 1–5, characterized
- 25 also by the fact that the final crystallization pressure is equal to atmospheric pressure. 25
7. Continuous method for obtaining pure terephthalic acid and glycol, starting from polyethylene terephthalate waste, in accordance with what is claimed in clauses 1–5, characterized also by the fact that the final crystallization pressure is lower than atmospheric pressure but greater than 1 mm Hg absolute, using a vacuum device.
- 30 8. Continuous method for obtaining pure terephthalic acid and glycol, starting from 30
polyethylene terephthalate waste, in accordance with what is claimed in clauses 1–5, also characterized by the fact that the final crystallization pressure is greater than the atmospheric pressure but less than 15 atmosphere.
9. Continuous method for obtaining pure terephthalic acid and glycol, starting from
- 35 polyethylene terephthalate waste, in accordance with what is claimed in clauses 1–4, characterized 35
also by the fact that the cooling is carried out by means of a cold surface, such as a jacket in the crystallizer, or by means of a coil in the crystallizer, or using both a jacket and a coil.
10. Continuous method for obtaining pure terephthalic acid and glycol, starting from polyethylene terephthalate waste, in accordance with what is claimed in clauses 1–4, also
- 40 characterized by the fact that the cooling is carried out by means of any combustion of a cold 40
surface and a simultaneous venting of the pressure.
11. Continuous method for obtaining pure terephthalic acid and glycol, starting from polyethylene terephthalate waste, in accordance with what is claimed in clauses 1–10, also characterized by the fact that the crystallization time is between 5 minutes and 5 hours.